Toward Photoswitchable Dendritic Hosts. Interaction between Azobenzene-Functionalized Dendrimers and Eosin

Andreas Archut,[1a] Gianluca Camillo Azzellini,[1b,c] Vincenzo Balzani,*[,1b] Luisa De Cola,[1b] and Fritz Vögtle*[,1a]

Contribution from the Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk Strasse 1, D-53121 Bonn, Germany, and Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, I-40126 Bologna, Italy

Received June 26, 1998

Abstract: Two poly(propyleneimine) dendrimers bearing up to 32 photoisomerizable azobenzene groups in the periphery have been used as potential hosts for eosin Y (2′,4′,5′,7′-tetrabromofluorescein dianion). The all-*E* azobenzene dendrimers can be reversibly switched to their *Z* form by light excitation. Both the *E* and *Z* forms of the dendrimers quench the eosin fluorescence by a static mechanism. The quenching is most likely due to an electron-transfer reaction between the singlet excited state of eosin and the tertiary amine units present along the branches of the dendrimers. Quenching by the *Z* form of the dendrimers is more efficient than quenching by the *E* form. The $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerization reactions of the azobenzene units of the dendrimers are sensitized by eosin via a triplet−triplet energy transfer mechanism. The results obtained indicate that eosin is hosted by the dendrimers and suggest that the *Z* forms are more efficient hosts than the *E* forms.

Introduction

Cascade molecules,[2] nowadays commonly called dendrimers,[3] are well-defined, highly branched macromolecules constructed from an initiator core upon which radially branched layers, termed generations, are covalently attached. Potentially important practical applications of dendrimers are related to the possibility of encapsulating guest molecules.[4] Examples of dynamic[5] and static[4] guest encapsulation have already been reported. In particular, Meijer et al.[4,6] have shown that when poly(propyleneimine) dendrimers bearing a bulky shell of 64 amino acids in the periphery (dendritic boxes) are constructed in the presence of guest molecules, such molecules can be irreversibly imprisoned into internal cavities of the dendrimer and then site-selectively liberated by suitable chemical reactions.[7]

For practical applications (e.g., drug delivery), a dendritic box should be opened and closed reversibly by means of a simple, external stimulus. Light is a particularly useful and efficient stimulus to cause reversible structural changes in molecular and supramolecular systems.[8] We are therefore engaged in a research program aimed at the synthesis and characterization of dendrimers containing light switchable units.[9]

It is well-known that azobenzene-type compounds undergo an efficient and fully reversible photoisomerization reaction.[10] For this reason, they have been extensively used to construct photoswitchable devices.[8,11] We have found that the thermodynamically stable *E* isomers of the azobenzene groups contained in the periphery of poly(propyleneimine) dendrimers (*para*, **P**, and *meta*, **M**, carboxamide substituted; first, **G1**, and fourth, **G4**, generations; Figure 1) are reversibly switched to the *Z* form by 313 nm light and can then be converted back to the *E* form by irradiation with 254 nm light or by heating.[9] Other research groups have investigated the isomerization of dendrimers containing an azobenzene as the central linker.[12]

Isomerization of azobenzene units involves a large structural rearrangement (Figure 2a). In going from the *E* to the *Z* isomer, the distance between the *para* carbon atoms of azobenzene decreases from 9 to 5.5 Å and the dipole moment increases from 0 (since the *E* form is planar and symmetric) to 3.0 D.[10b] Structural changes in the peripheral units of a dendrimer (Figure 2b) can modify the surface properties and, in large architectures, can also cause rearrangements in the internal cavities. For all these reasons, we thought that dendrimers bearings azobenzene

(1) (a) Bonn University. (b) University of Bologna. (c) On leave from the Instituto de Química, Universidade de São Paulo, C.P. 26077, São Paulo, Brazil.

(2) Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155.

(3) (a) Newkome, G. R.; Moorefield, C.; Vögtle, F. *Dendritic Macromolecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, 1996. (b) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 193. (c) Gorman, C. *Adv. Mater*. **1998**, *10*, 295.

(4) Jansen, J. F. G. A.; de Brabander-van der Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226.

(5) (a) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (b) Turro, C.; Niu, S.; Bossmann, S. H.; Tomalia, D. A.; Turro, N. J. *J. Phys. Chem.* **1995**, *99*, 5512. (c) Naylor, A. M.; Goddard, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc*. **1989**, *111*, 2339.

(6) Jansen, J. F. G. A.; Meijer, E. W. *J. Am. Chem. Soc.* **1995**, *117*, 4417.

(7) See also: Miklis, P.; Cagin, T.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1997**, *119*, 7458.

(8) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, 1991. Balzani, V.; Scandola, F. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 10, p 687.

(9) Archut, A.; Vögtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, V.; Ramanujam, P. S.; Berg, R. H. *Chem. Eur. J.* **1998**, *4*, 669.

(10) (a) Rau, H. In *Photochromism, Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; Chapter 4. (b) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915.

(11) (a) Shinkai, S.; Manabe, O. *Top. Curr. Chem.* **1984**, *121*, 67. (b) Shinkai, S. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 1, p 671.

(12) (a) Junge, D. M.; McGrath, D. V. *Chem. Commun.* **1997**, 857. (b) Jiang, D.-L.; Aida, T. *Nature* **1997**, *388*, 454.

10.1021/ja9822409 CCC: $15.00
Published on Web 12/02/1998

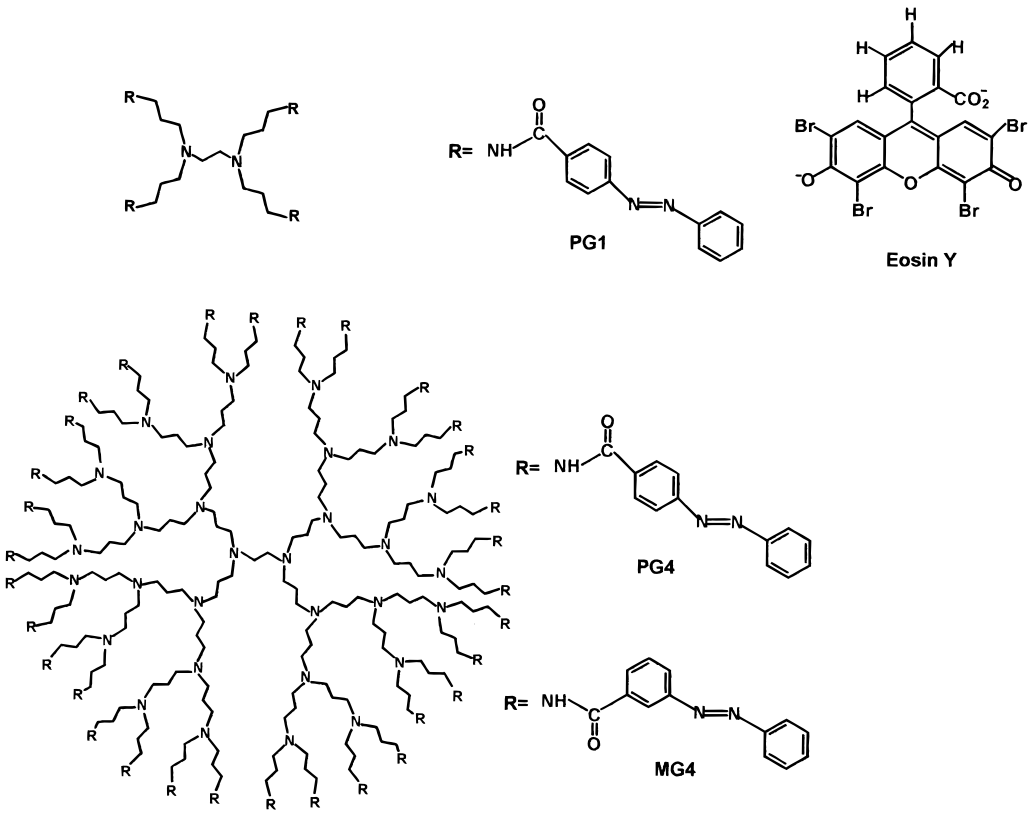

Figure 1. First (**G1**) and fourth (**G4**) generation dendrimers. **P** and **M** indicate *para* and *meta* carboxamide substitution. The structure of eosin is also shown.

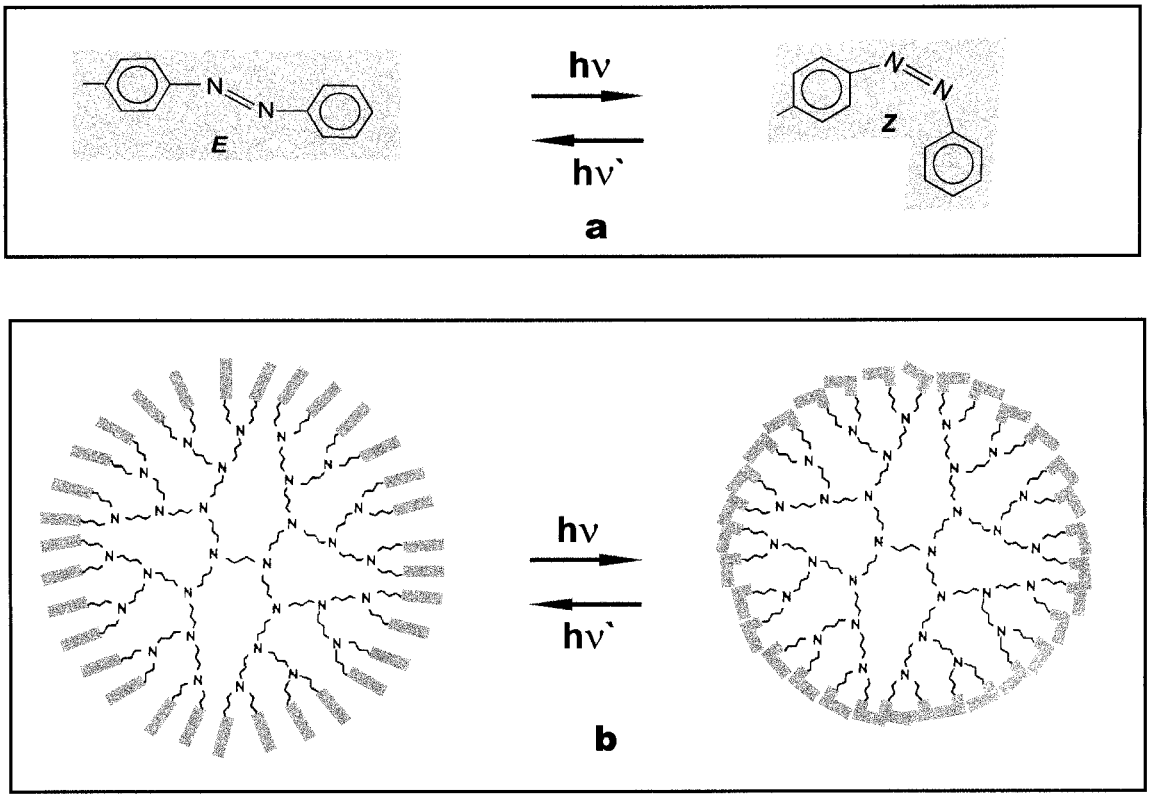

Figure 2. Photoisomerization of azobenzene and of the fourth generation dendrimers bearing 32 photoisomerizable azobenzene groups in the periphery.

groups in the periphery could play the role of photoswitchable hosts.

To investigate this possibility, we have examined the photochemical and photophysical properties of solutions containing dendrimers and the potential host eosin Y (2′,4′,5′,7′-tetrabromofluorescein dianion; hereafter simply called eosin, Figure 1). The reason for choosing eosin was 2-fold: (i) its strong fluorescence,[13] which could be affected in case of

inclusion in the dendrimer, and (ii) the energy of its lowest triplet state,[13] which is higher than that of the lowest azobenzene triplet state[14] and could therefore sensitize the photoisomerization reactions of the peripheral units of the dendrimer.

Experimental Section

All the experiments were carried out in dimethylformamide (DMF) solution at 293 K, unless otherwise noted. The preparation and characterization of the dendrimers and the equipment used were described in a previous paper.[9,15]

Procedure. To perform quenching and sensitization experiments and to compare the results obtained with molecules as different as azobenzene and the fourth generation dendrimers which contain up to 32 azobenzene units, we chose very carefully the experimental conditions. Limitations were imposed by (i) the need to use the same irradiation wavelength to minimize experimental errors on the rate of the photochemical reactions, (ii) a partial overlap between the spectra of eosin and azobenzene chromophoric groups at the irradiation wavelength (vide infra), (iii) the need to use spectrophotometric analysis to follow the photoisomerization reaction,[10] and (iv) self-association of eosin molecules at high concentrations.[16] The conditions in which the experimental errors could be minimized were as follows: eosin concentration 5.0×10^{-6} M and azobenzene concentration 1.6×10^{-3} M, corresponding to an absorbance of 0.95 at 450 nm. To keep constant the number of azobenzene units in the experiments involving the G1 and G4 dendrimers, the concentration of the dendrimers was adjusted so as to have the same absorbance of the 1.6×10^{-3} M azobenzene solutions. This means that the theoretical[15] concentration of the G1 and G4 dendrimers was 4.0×10^{-4} and 5.0×10^{-5} M, respectively.

Correction of eosin fluorescence intensity for inner filter effects was performed as indicated in the literature.[17,18] Irradiation was performed at 365 nm for the conversion of the *E* to the *Z* form and at 545 nm for the study of the kinetics of the $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerization processes. The reactions were followed by the absorbance changes in the maximum of the n$-\pi^*$ absorption bands (450 and 435 nm for the *E* and *Z* form, respectively). In the direct photoisomerization experiments, the initial absorbance of the solution was <0.1, so that the photochemical reactions followed a first-order rate law. The photosensitization of the isomerization reaction by excited eosin was a pseudo-first-order process since its rate depended on the concentration of the azobenzene species.

Experiments on solutions containing concentrations of the various species different from those stated above were not performed because of the large experimental errors expected and the impossibility of making direct comparisons with experiments carried out in the selected conditions.

Results and Discussion

Absorption Spectra. The absorption spectrum in the visible region of a 5.0×10^{-5} M solution of the fourth generation *para*-carboxamine-substituted azobenzene dendrimer bearing up to 32 azobenzene units in the *E* form (*E*-**PG4**) is shown in Figure 3 (curve a). The band with $\lambda_{max} = 450$ nm ($\epsilon = 1.9 \times 10^4$ M^{-1} cm^{-1}) is due to the n$\rightarrow\pi^*$ transition of the azobenzene units.[10] The spectrum of 5.0×10^{-6} M eosin in DMF solution is shown in Figure 3 (curve b). The intense band in the visible region ($\lambda_{max} = 535$ nm; $\epsilon = 1.0 \times 10^5$ M^{-1} cm^{-1}) is slightly affected by concentration because of formation of molecular aggregates.[16] The spectrum of a solution containing both *E*-**PG4** and eosin (Figure 3, curve c) is identical, within experimental error, to the sum of the spectra of the two separated compounds. Upon irradiation of the *E*-**PG4** solution with 365 nm light, a photostationary state is reached in which more than 95% of the azobenzene groups are in their *Z* form. The spectrum of a solution containing 5.0×10^{-5} M *Z*-**PG4** and 5.0×10^{-6} M eosin (Figure 3, curve d) is again identical, within experimental error, to the sum of the spectra of the two separated compounds. Similar results have been obtained in the case of *E*-**MG4** and *Z*-**MG4**. These results show that the interaction between the two species, if any, is clearly too weak to affect the absorption spectra.

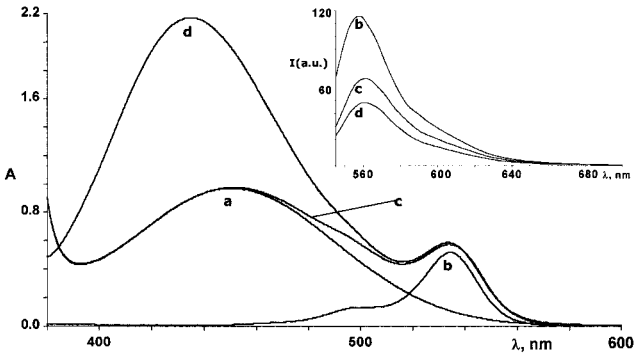

Figure 3. Absorption spectra of DMF solutions containing (a) 5.0×10^{-5} M *E*-**PG4**, (b) 5.0×10^{-6} M eosin, (c) 5.0×10^{-5} M *E*-**PG4** and 5.0×10^{-6} M eosin, and (d) 5.0×10^{-5} M *Z*-**PG4** and 5.0×10^{-6} M eosin. The inset shows the fluorescence band of solutions containing eosin alone (curve b) and eosin in the presence of *E*-**PG4** and *Z*-**PG4** (curves c and d, respectively).

Table 1. Quenching of the Eosin Fluorescence[a]

compd	*E* form	*Z* form
azobenzene[b]	97	100
PG1[c]	92	90
PG4[d]	67	50
MG4[d]	90	66

[a] Corrected fluorescence intensities, compared to the fluorescence intensity of eosin alone taken as 100%. Eosin concentration, 5.0×10^{-6} M. DMF solution, 293 K. The experimental error is estimated to be 5%. [b] 1.6×10^{-3} M. [c] 4.0×10^{-4} M. [d] 5.0×10^{-5} M.

Quenching of Eosin Fluorescence. Eosin displays a strong fluorescence band in the red region of the spectrum (in water: $\lambda_{max} = 570$ nm, $\Phi = 0.69$, $\tau = 3.6$ ns;[10] in DMF: $\lambda_{max} = 560$ nm, $\tau = 3.8$ ns). The inset to Figure 3 shows the fluorescence band of solutions containing eosin alone (curve b) and eosin in the presence of *E*-**PG4** and *Z*-**PG4** (curves c and d, respectively). Clearly, the intensity of the fluorescence band is much smaller when the dendrimers are present. When the *E*-**PG4** and *Z*-**PG4** dendrimers were replaced by 32 times more concentrated azobenzene (to keep the number of azobenzene units approximately constant), no quenching was observed within the experimental error. The corrected fluorescence intensity data obtained for the examined compounds are shown in Table 1. As one can see, the quenching is smaller for the first generation dendrimer, whose concentration was 8 times higher than that

(13) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Dekker: New Yok, 1993.

(14) Ronayette, J.; Arnaud, R.; Lemaire, J. *Can. J. Chem.* **1974**, *52*, 1858.

(15) A certain polydispersity, particularly of the higher generations originating from imperfections of the polyamine dendrimer skeletons, cannot be eliminated with the current workup procedures. MALDI-TOF mass spectroscopy does not show peaks that could be attributed to impurities originating from structural defects of the polyamine precursor or from incomplete conversion with the activated esters up to generation 3. In the case of generation 4 there are additional peaks below the molecule ion peak that originate from imperfect polyamine starting material, that is dendritic polyamines with less than 32 propylene amine arms in the periphery. For the sake of reliability of the photochemical investigations we have thus not extended our study to generation 5 azobenzene dendrimers. Structural defects in poly(propyleneimine) dendrimers have been investigated and categorized recently: Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Nepogodiev, S. A.; Meijer, E. W.; Peerlings, H. W. I.; Stoddart, J. F. *Chem. Eur. J.* **1997**, *3*, 974. Hummelen, J. C.; van Dogen, J. L. J.; Meijer, E. W. *Chem. Eur. J.* **1997**, *3*, 1493.

(16) Valdes-Aguilera, O.; Neckers, D. C. *Acc. Chem. Res.* **1989**, *22*, 171.

(17) Lakowicz, J. H. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1986; Chapter 2.

(18) Credi, A.; Prodi, L. *Spectrochim. Acta A* **1998**, *54*, 159.

of the fourth generation compounds. In the assumption of a dynamic quenching mechanism, we can use the Stern−Volmer equation[19] to evaluate the quenching constants. With use of the data of Table 1, the measured eosin lifetime, and the concentration of the fourth generation dendrimers, values in the range of 5×10^{11} to 5×10^{12} M^{-1} s^{-1} are obtained, which are much higher than the diffusion controlled limit (about 7×10^9 M^{-1} s^{-1} for DMF solution at 298 K).[13] This, of course, shows that a dynamic quenching mechanism is implausible. Furthermore, in the case of a dynamic mechanism, the fluorescence lifetime should be affected in parallel with the fluorescence intensity,[19] but we found that the quenching of the fluorescence intensity by the fourth generation dendrimers is not accompanied by any change in the fluorescence lifetime. These results clearly show that the observed fluorescence quenching does not occur by diffusion, but by a static mechanism implying association between the eosin and dendrimer.

The static quenching of the eosin fluorescence intensity in the presence of the dendrimers could be due either to a change in the rate constants of the intrinsic radiative and/or nonradiative deactivation processes of the dye caused by the different "solvation" enviroment in the dendrimer pockets or to a true quenching process by energy or electron transfer. In the first case, however, the fluorescence lifetime would most likely change, contrary to what we observed. Therefore, we consider the possibility of a static energy or electron-transfer quenching. The fluorescent excited state of eosin (whose energy is 2.17 eV)[13] lies below the lowest singlet excited state of the azobenzene units, as it clearly appears from the absorption spectra shown in Figure 3. Therefore, quenching of the eosin fluorescent singlet excited state by energy transfer to the azobenzene chromophoric units would imply formation of triplet azobenzene, a process which, being spin forbidden for both Coulombic and exchange energy transfer, is likely too slow to compete with the short lifetime (3.8 ns) of the excited eosin singlet. On the other hand, energy transfer to the amine units present in the branches of the dendrimer is not possible because such units do not have energy levels which lie below the excited eosin singlet.

As far as electron-transfer quenching is concerned, it should be pointed out that both eosin and azobenzene are relatively difficult to oxidize and to reduce (for eosin in water, $E°(\text{Eos}/\text{Eos}^-) = -0.85$ V, $E°(\text{Eos}^+/\text{Eos}) = +1.1$ V;[20] for azobenzene, $E°(\text{Az}/\text{Az}^-) = -1.36$ V vs SCE in DMF,[21] whereas no oxidation process is reported in the literature). Since the energy of the fluorescent excited state of eosin is only 2.17 eV, a fast electron-transfer quenching reaction involving the azobenzene units does not seem plausible since, judging from the above-mentioned electrochemical data, both the reductive and the oxidative quenching processes do not appear to be exergonic.[22] The amine units present in the branches of the dendrimer, however, are easily oxidized. Triethylamine, which is a good model for the amine units of the dendrimers, undergoes an irreversible oxidation process with $E_p = +0.65$ V vs $Ag-AgNO_3$.[21] On the basis of the excited-state energy and electrochemical data, the reductive quenching of the excited state of eosin by the amine units is considerably exergonic[22] and it can therefore account for the observed quenching process.[23]

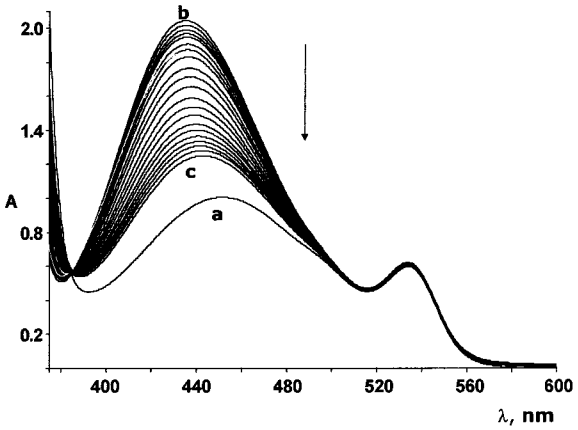

Figure 4. Curve a is the spectrum of a solution containing 5.0×10^{-5} M *E*-**PG4** and 5.0×10^{-6} M eosin. Curve b is the spectrum recorded after prolonged irradiation of the *E* form at 365 nm, when the photostationary state containing >90% *Z* form is obtained. Curve c is the spectrum obtained upon excitation of the *Z* form at 545 nm up to a new photostationary state. Leaving the solution in the dark, curve c goes back to curve a because the fraction of *Z* form present in the photostationary state under 545 nm excitation is transformed to the stable *E* form.

In any case, the important point is that fluorescence quenching occurs by a static mechanism, so that we can conclude that the quenchable eosin molecules are hosted inside the dendrimer. The results obtained (Table 1) show that the minimum value for the fraction of eosin molecules hosted in *Z*-**PG4** is 50%. It is interesting to note that for both the **PG4** and **MG4** dendrimers the quenching ability (which is related to the hosting ability) of the *Z* form is higher than that of the *E* form.

Direct and Eosin-Sensitized Photoisomerization of the Azobenzene Units. Irradiation of *E*-**PG4** in DMF solution with 545 nm light caused the $E \rightarrow Z$ isomerization reaction of the azobenzene units. For short irradiation times (i.e., until there is no appreciable absorption by the Z isomer product), the reaction was first order, with a rate constant of 6.3×10^{-3} min^{-1}. Irradiation of a solution containing 5.0×10^{-5} M *Z*-**PG4** and 5.0×10^{-6} M eosin, where the 545 nm excitation light is absorbed by both components (Figure 3, curve c), caused a pseudo-first-order isomerization reaction with a rate constant of 9.7×10^{-3} min^{-1}. The increase in the rate constant compared to the direct photoreaction indicates that the light absorbed by eosin is effective to cause isomerization. Similar experiments were carried out for other compounds, for the back $Z \rightarrow E$ photoisomerization ($\lambda_{\text{irradiation}} = 545$ nm, Figure 4), and for both aerated and deaerated solutions. The results obtained, gathered in Table 2, show that (i) all the compounds undergo direct $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerization, (ii) the light absorbed by eosin is effective to promote the photoisomerization reactions (sensitized photoisomerization), (iii) the sensitized reaction is more efficient in the case of the $Z \rightarrow E$ isomerization, as it usually happens for azobenzene-type compounds,[10,24] (iv) the efficiency of the sensitized reaction is different for the various compounds

(19) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, 1978. (b) Gilbert, A.; Baggot, J. *Essentials of Molecular Photochemistry*; Blackwell: Oxford, 1991.

(20) Moser, J.; Grätzel, M. *J. Am. Chem. Soc.* **1984**, *106*, 6567.

(21) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Dekker: New York, 1970.

(22) For an excited-state electron-transfer reaction

$$A^* + B \rightarrow A^- + B^+ \text{ (reductive quenching)}$$

the thermodynamic driving force can be estimated from the approximate equation:

$$\Delta G° = -\Delta E°° - E(A/A^-) + E(B^+/B)$$

where $E(A/A^-)$ and $E(B^+/B)$ are the energies (in eV) of the one-electron-reduction processes, and $\Delta E°°$ is the excited-state spectroscopic energy.[19] An equivalent equation can be written for the oxidative quenching.

(23) Photosensitized oxidation of tertiary aliphatic amines by eosin has been observed: Bartholomeu, R. F.; Davidson, R. S. *J. Chem. Soc. (C)* **1971**, 2347.

Table 2. Photoisomerization Reactions[a]

	$E \rightarrow Z$		$Z \rightarrow E$	
compd	direct[b]	sensitized[c]	direct[b]	sensitized[c]
azobenzene	3.6 (3.4)	8.6 (7.2)	4.3 (4.0)	18 (12)
PG1[d]	5.9 (5.5)	7.6 (6.6)	8.0 (8.0)	24 (14)
PG4[e]	6.3 (6.7)	9.7 (7.5)	9.8 (9.8)	26 (18)
MG4[f]	3.8 (3.5)	8.3 (6.4)	4.5 (5.7)	25 (11)

[a] Initial pseudo-first-order rate constant $\times 10^3$ min^{-1}. Deaerated DMF solutions, 293 K. Excitation with 545 nm light. Maximum conversion, 7−10%. Values in parentheses refer to air-equilibrated solutions. The experimental error is estimated to be 10%. [b] Initial fraction of absorbed light: 61%. [c] Eosin concentration: 5.0×10^{-6} M. Initial fraction of absorbed light: eosin, 56%; azobenzene units, 12%. [d] 1.6×10^{-3} M. [e] 4.0×10^{-4} M. [f] 5.0×10^{-5} M.

(vide infra), and (v) the rate constant of the sensitized photoisomerization reaction depends on the presence of dioxygen, whereas this is not the case for the direct photoreaction. These observations show that, from a qualitative viewpoint, the azobenzene units of the dendrimers behave like free azobenzene molecules.[10]

As mentioned above, the rate constants reported in Table 2 for the direct photoreactions have been obtained with exactly the same absorbance at the excitation wavelength for all compounds to minimize the experimental errors. This means that the same number of azobenzene units were present in each case, but the concentration of the fourth generation dendrimers was 8 times lower than that of the first generation dendrimers and 32 times lower than that of azobenzene. Even under such "normalized" conditions, the values of the rate constants cannot be directly compared because it is known that the quantum yield of the direct photoreaction of azobenzene-type compounds is influenced by ring substituents. Therefore, only the data for **PG1** and **PG4** are really homogeneous and the fact that they are substantially the same indicates that the dendrimer dimensions have no effect on the direct photoisomerization reactions of the azobenzene-type units.

In the photosensitized reactions, the eosin concentration was constant and the concentration of the fourth generation dendrimers was again 8 times lower than that of the first generation dendrimers and 32 times lower than that of azobenzene. Under such conditions, the fractions of incident light absorbed by eosin (56%) and by the azobenzene units (12%) were the same in all experiments. At first sight, the fact that the rate constants are very close in all cases (in particular, practically equal for PG1 and PG4) might appear unreasonable because of the different concentrations of the acceptor species involved in the energy transfer process. The simplest explanation is that the eosin triplet is so long-lived[13] that it is completely scavenged in all cases. Another possibility is that there is an effect related to the dendrimer dimension that counterbalances the differences in concentration. For example, in the larger dendrimers eosin triplets may be more effective because, as shown by the fluorescence quenching experiments, there are eosin molecules contained in the dendrimer cavities which might have a higher probability to react with azobenzene units compared to what would happen in a normal diffusion process. Unfortunately, experimental difficulties related to the components of our systems (see above) did not allow us to investigate this problem.

(24) In the case of azobenzene, sensitization by triplet energy transfer is very efficient ($\Phi = 1$) for the $Z \rightarrow E$ and very inefficient ($\Phi = 0.015$) for the $E \rightarrow Z$ reaction: Bortolus, P.; Monti, S. *J. Phys. Chem.* **1979**, *83*, 648.

Conclusions

We have found that in DMF solutions containing eosin and poly(propyleneimine) dendrimers of the fourth generation bearing up to 32 photoisomerizable azobenzene groups in the periphery (i) the lowest singlet, fluorescent excited state of eosin is quenched by the amine units contained in the branches of the dendrimers and (ii) and the $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerization reactions of the peripheral azobenzene units are sensitized by triplet eosin. The fluorescence quenching experiments show that eosin is hosted in the dendrimers and suggest that the *Z* forms of the fourth generation dendrimers are better hosts than the *E* forms.

Acknowledgment. This work was supported in Germany by Volkswagen Stiftung and in Italy by MURST (Supramolecular Devices Project) and the University of Bologna (Funds for Selected Research Topics). G.C.A. wishes to thank Fapesp (Fundação de Amparo à Pesquisa do Estado de São Paulo—Brazil) for financial support.

JA9822409